

Electronic Supplementary Information (20 pages)

Incorporation of active metal sites in MOFs *via in situ* generated ligand deficient metal-linker complexes

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Section S1 *Materials and General Procedures*

All solvents and reagents were purchased commercially and, unless otherwise noted, were used without further purification. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. FTIR spectra were obtained by using a Bio-Rad FTS-45 FTIR spectrometer. The powder XRD patterns were obtained with a Bruker D8 Advance system equipped with a Cu sealed tube ($\lambda = 1.5406 \text{ \AA}$). The following conditions were applied: 40 kV, 40 mA, increment = 0.007° , scan speed = 1.5 s / step. The simulated powder patterns were calculated from the single crystal X-ray diffraction data and generated with Mercury 2.3 software. All TGA experiments were performed under a N_2 atmosphere from 25 - 800 °C at a temperature ramp rate of 5 °C / min.

Section S2 *Synthesis*

Synthesis of MOF-647A and MOF-648:

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (2.76 g, 11.45 mmol) and 1*H*-pyrazole-3,5-dicarboxylic acid (0.72 g, 4.15 mmol) were dissolved in 100 mL of *N,N*-dimethylformamide (DMF) and the clear solution was divided in ten 20 mL vials. After they were tightly capped the vials were heated to 100 °C at a rate of 2 °C/min for 20 h in an isothermal oven. A mixture of light green thin-plate and dark blue-green block crystals was removed from the vial containing the mother liquor and washed with DMF ($3 \times 5 \text{ mL}$). The mixture of crystalline compounds was purified and separated by (a) sonicating, (b) filtering, (c) washing with DMF, and (d) depositing in a separation funnel, followed by the addition of 17.3:11 (v:v) CH_2Br_2 :DMF.^[S1] Because of the density difference of the two type of crystals, the light green thin-plate crystals of MOF-647A (450 mg) float to the top of the solution, while the dark blue-green block crystals of MOF-648 (480 mg) stay at the bottom. Elemental analysis calcd (%) for $\text{C}_{15.71}\text{H}_{21.51}\text{Cu}_3\text{N}_{5.90}\text{O}_{13}$ (MOF-647A) = $[\text{Cu}_3(\text{L})_2 \cdot (\text{DMF})_{1.9}(\text{H}_2\text{O})_{3.1}]$ (L = pyrazole-3,5-dicarboxylate): C 27.28, H 3.13, N 11.95; found: C 26.80, H, 3.28, N 11.5. IR (KBr, cm^{-1}): for MOF-647A: 3117 (br), 1636 (m), 1582 (s), 1451 (s), 1384 (s), 1335 (s), 1281 (s), 1102 (m), 1057 (s), 1017 (s), 849 (s), 775 (s), 671 (m), 628 (w).

Elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{85}\text{Cu}_{12}\text{N}_{27}\text{O}_{45}$ (MOF-648) = $[\text{Cu}_{12}(\text{L})_8(\text{DMF})_9] \cdot (\text{DMF})_2(\text{H}_2\text{O})_2$: C 31.06, H 3.03, N 13.4; found: C 28.60, H 3.25, N 12.70. IR (KBr, cm^{-1}): for MOF-648: 3167 (br), 1636 (w), 1583 (m), 1514 (w), 1384 (s), 1335 (m), 1282

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(m), 1102 (m), 1058 (s), 1017 (m), 847 (m), 775 (s), 671 (w), 626 (m). The volatility of the co-crystallized solvents in the samples contributes to the discrepancy in the elemental analyses.

Single phase preparation of MOF-647A.

Cu(NO₃)₂·2.5H₂O (0.276 g, 1.145 mmol) and 1*H*-pyrazole-3,5-dicarboxylic acid (0.072 g, 0.415 mmol) were dissolved in 8 ml of DMF in a 20 mL glass vial. After the vials were tightly capped they were heated to 75 °C at a rate of 2 °C/min for 48 h in an isothermal oven. Thin plate blue crystals were removed from the mother liquor contained in the vial and washed with DMF (3 × 5 mL). Elemental analysis calcd (%) for C_{15.71}H_{21.51}Cu₃N_{5.90}O₁₃ (MOF-647A) = C 27.28, H 3.13, N 11.95; found: C 26.80, H, 3.28, N 11.5.

Single phase preparation of MOF-648.

Cu(NO₃)₂·2.5H₂O (0.13 g, 0.57 mmol) and 1*H*-pyrazole-3,5-dicarboxylic acid (0.05 g, 0.28 mmol) were dissolved in 20 mL of DMF in a 50 mL glass vial. After they were tightly capped the vials were heated to 100 °C at a rate of 1 °C/min for 12 h in an isothermal oven. Dark blue-green block crystals were removed from the mother liquor contained in a vial and washed with DMF (3 × 5 mL). Elemental analysis calcd (%) for C₇₃H₈₅Cu₁₂N₂₇O₄₅ (MOF-648) = C 31.06, H 3.03, N 13.40; found: C 29.5, H 3.94, N 13.36. The volatility of the co-crystallized solvents in the samples contributes to the discrepancy in the elemental analyses. IR (KBr, cm⁻¹): for MOF-648: 3167 (br), 1636 (w), 1583 (m), 1514 (w), 1384 (s), 1335 (m), 1282 (m), 1102 (m), 1058 (s), 1017 (m), 847 (m), 775 (s), 671 (w), 626 (m).

Preparation of MOF-647B.

About 50 mg of the as-prepared form of MOF-647A was thoroughly washed with fresh DMF followed by washing with anhydrous THF (5 × 5 mL). The THF washed material was then soaked in fresh anhydrous THF for 3 days with fresh THF added every 24 h.

Section S3 Crystallographic Data

Single X-Ray Diffraction Studies on MOF-647A, MOF-647B and MOF-648

Crystallographic data for all the MOFs were collected on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoK α radiation, $\lambda = 0.71073 \text{ \AA}$)^[S2] at 183(2) K. The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, analytical absorption corrections,^[S3] and data reduction were performed with the Oxford program suite *CrysAlisPro*.^[S4] The structures were solved with the Patterson (heavy atom) method and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.^[S5] All programs used during the crystal structure determination process are included in the WINGX software.^[S5] The program PLATON^[S6] was used to check the results of the X-ray analyses. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC-829034 for MOF-647A, CCDC-829035 for MOF-647B and CCDC-829036 for MOF-648. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In MOF-647A one Cu atom is five-coordinated by three O atoms and two N atoms while the second Cu atom is five-coordinated by four O atoms and one N atom. The latter Cu atom is either coordinated by a DMF molecule or a water molecule with site-occupancy factors of 0.451(6) and 0.549(6), respectively. The central Cu(2) atom lies on a crystallographic two-fold axis. Some restraints and constraints were used to correct the thermal parameters of the disordered Cu-coordinated DMF molecule and the positions of the water H atoms (EADP, DFIX and DANG commands in *SHELXL97*). All other H positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and with C-H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

In MOF-647B one Cu atom is five-coordinate by two N atoms, two carboxylate O atoms and one O atom from a THF molecule. The other Cu atom is either four-coordinated or five-coordinated depending on the orientation of the disordered THF (site-occupancy factor *sof* of 0.5). The water H atoms were located in a difference Fourier map but they were refined with fixed coordinates and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H positions were calculated after each cycle

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of refinement using a riding model, with C-H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and with C-H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms.

In MOF-648 two Cu atoms exhibit a square-planar geometry (coordinated by four O atoms), one Cu atom is five-coordinated by three O atoms and two N atoms, and one Cu atom is either fix-coordinated by three O atoms and two N atoms or six-coordinated by four O atoms and two N atoms depending on the orientation of the disordered DMF (site-occupancy factor *sof* of 0.25). The three-dimensional framework contains three Cu-coordinated DMF molecules while cavities are occupied by solvent molecules of DMF (*sof* = 1) and water (disordered molecules with *sof* = 0.5). Some restraints and constraints were used to correct the geometry and thermal parameters of the isolated and disordered DMF molecules (EADP and SAME commands in *SHELXL97*). All H positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and with C-H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The water H atoms could not be located and were not introduced in the model.

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Table S1. Summary of the X-ray diffraction studies of MOF-647A, MOF-647B and MOF-648.

	MOF-647A	MOF-647B	MOF-648
empirical formula	C _{15.71} H _{21.51} Cu ₃ N _{5.90} O ₁₃	C ₁₈ H ₂₂ Cu ₃ N ₄ O ₁₂	C ₇₃ H ₈₅ Cu ₁₂ N ₂₇ O ₄₅
formula weight (g·mol ⁻¹)	691.65	677.05	2823.28
temperature (K)	183(2)	183(2)	183(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system, space group	tetragonal, <i>I</i> 4 ₁ <i>acd</i>	tetragonal, <i>I</i> 4 ₁ <i>acd</i>	orthorhombic, <i>Pbcm</i>
<i>a</i> (Å)	17.6342(6)	17.1637(5)	15.3345(1)
<i>b</i> (Å)	17.6342(6)	17.1637(5)	14.5465(1)
<i>c</i> (Å)	33.4999(11)	34.0665(6)	26.2229(3)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
volume (Å ³)	10417.3(6)	10035.7(5)	5849.37(9)
Z, density (calcd) (Mg·m ⁻³)	16, 1.762	16, 1.792	2, 1.603
abs coefficient (mm ⁻¹)	2.499	2.587	2.224 mm
<i>F</i> (000)	5568.8	5456	2840
crystal size (mm ³)	0.13 × 0.09 × 0.05	0.19 × 0.10 × 0.04	0.34 × 0.23 × 0.17
θ range (deg)	2.43 to 25.68	2.66 to 25.68	2.48 to 30.51
reflections collected	24570	11076	87527
reflections unique	2480 / <i>R</i> _{int} = 0.141	2325 / <i>R</i> _{int} = 0.043	9101 / <i>R</i> _{int} = 0.072
completeness to θ (%)	99.9	97.2	99.9
absorption correction	analytical	analytical	analytical
max/min transmission	0.788 and 0.604	0.917 and 0.746	0.741 and 0.591
data / restraints / parameters	978 / 7 / 181	1155 / 0 / 158	6196 / 16 / 363
goodness-of-fit on <i>F</i> ²	0.738	0.921	1.037
final <i>R</i> ₁ and <i>wR</i> ₂ indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0399, 0.0800	0.0731, 0.2122	0.0535, 0.1738
<i>R</i> ₁ and <i>wR</i> ₂ indices (all data)	0.1357, 0.0930	0.1319, 0.2363	0.0773, 0.1820
largest diff. peak and hole (e·Å ⁻³)	0.382, -0.466	2.318, -0.906	2.375, -2.413

The unweighted *R*-factor is $R_1 = \sum(F_o - F_c) / \sum F_o$; *I* > 2 σ (*I*) and the weighted *R*-factor is $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$.

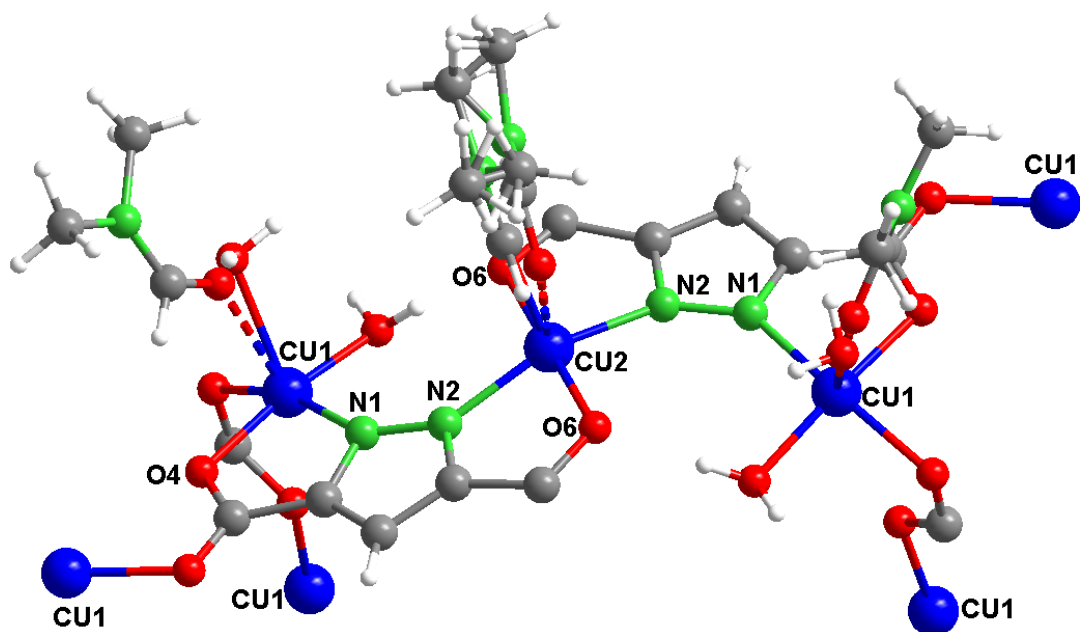


Fig. S1. A ball and stick presentation of the coordination environment of the trinuclear building unit in MOF-647A ($[\text{Cu}_3(\text{L})_2 \cdot (\text{DMF})_{1.9}(\text{H}_2\text{O})_{3.1}]$). The coordination of the disordered DMF and water solvents at Cu(1) with site-occupancy factor of 0.451(6) and 0.549(6) are shown in dashed and solid bonds respectively. In Cu(2), one of the disordered coordinated DMF with a site-occupancy factor of 0.5 is shown with a dashed bond. Color code: Cu, blue; N, green; O, red; C, gray; H, white. Selected atom labels are shown.

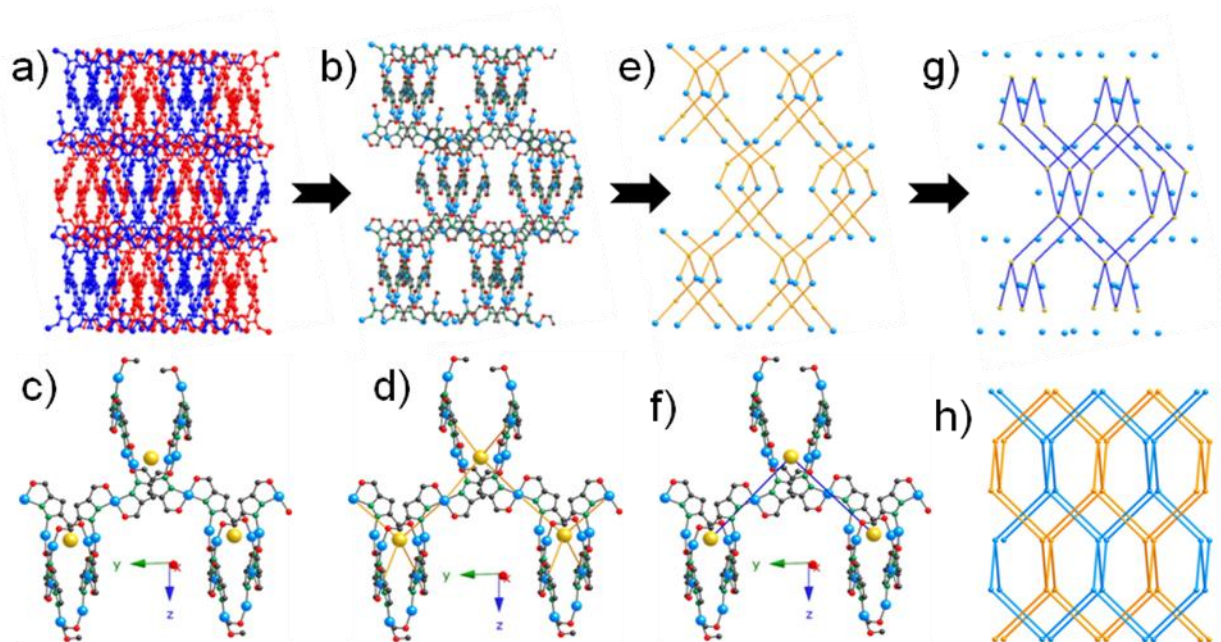


Fig. S2. Topological analysis of MOF-647A: Part of the doubly interpenetrated frameworks presented in a ball and stick model, where one of the frameworks is shown in blue and the other in red color (a); after removing the single blue net (b); to simplify the connectivity in (b), yellow spheres (near 4 Cu(1) atoms) could be displaced (c); after connecting the yellow spheres via Cu(2) (d), the simplified net (e) could be generated; to further simplify the overall 3D net (**dia**) connectivity (g), the connection through Cu(2) (since they do not take part in 3D connectivity) was ignored (f); schematic of the real doubly interpenetrated **dia** net (h). Coordinated guests and hydrogen atoms are omitted for clarity. Color code: Cu, blue; N, green; O, red; C, gray.

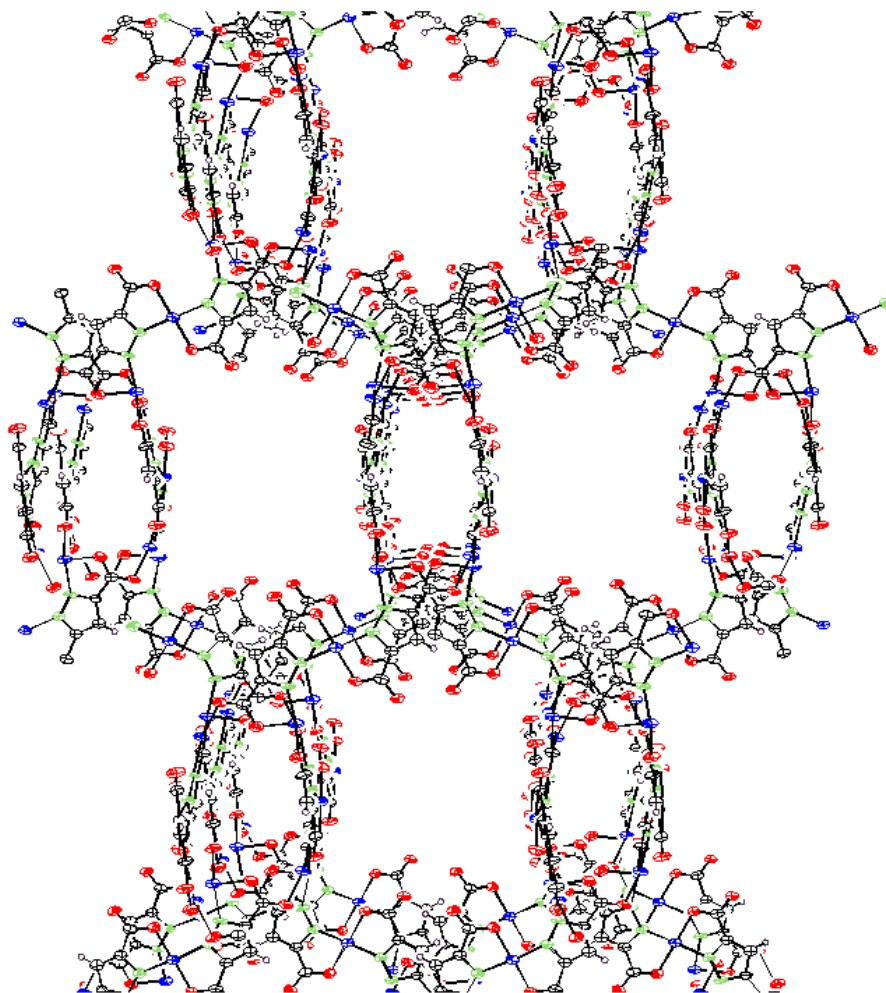


Fig. S3. ORTEP drawing (50% probability) of the part of the extended 3D structure of MOF-647A ($[\text{Cu}_3(\text{L})_2(\text{DMF})_{1.9}(\text{H}_2\text{O})_{3.1}]$) viewed down along the crystallographic *a* axis. Color code: Cu, blue; N, yellow-green; O, red; C, black; H, violet. Coordinated solvent molecules of DMF and H_2O are omitted for clarity.

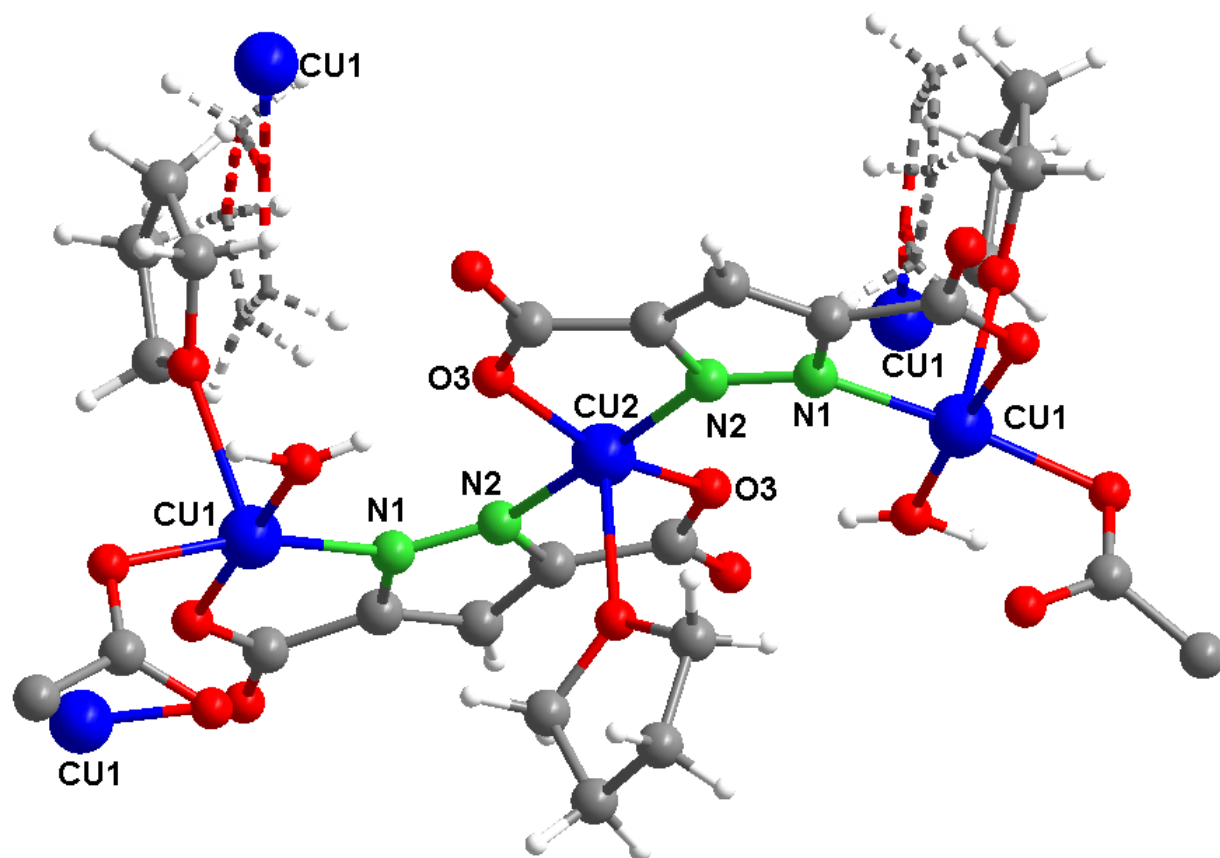


Fig. S4. A ball and stick presentation of the coordination environment of the trinuclear building unit in MOF-647B ($[\text{Cu}_3(\text{L})_2 \cdot (\text{THF})_2(\text{H}_2\text{O})_2]$). The central Cu(2) ion is doubly chelated by two pyrazolate ligands and the fifth coordination site is occupied by the THF molecule to fulfil the distorted square pyramidal geometry. Meanwhile each of the Cu(1) can either be considered as tetra or penta coordinated depending upon the orientation of the THF molecules. One of the orientations of the THF molecule is represented with dotted lines. Color code: Cu, blue; N, green; O, red; C, gray; H, white. Selected atom labels are shown.

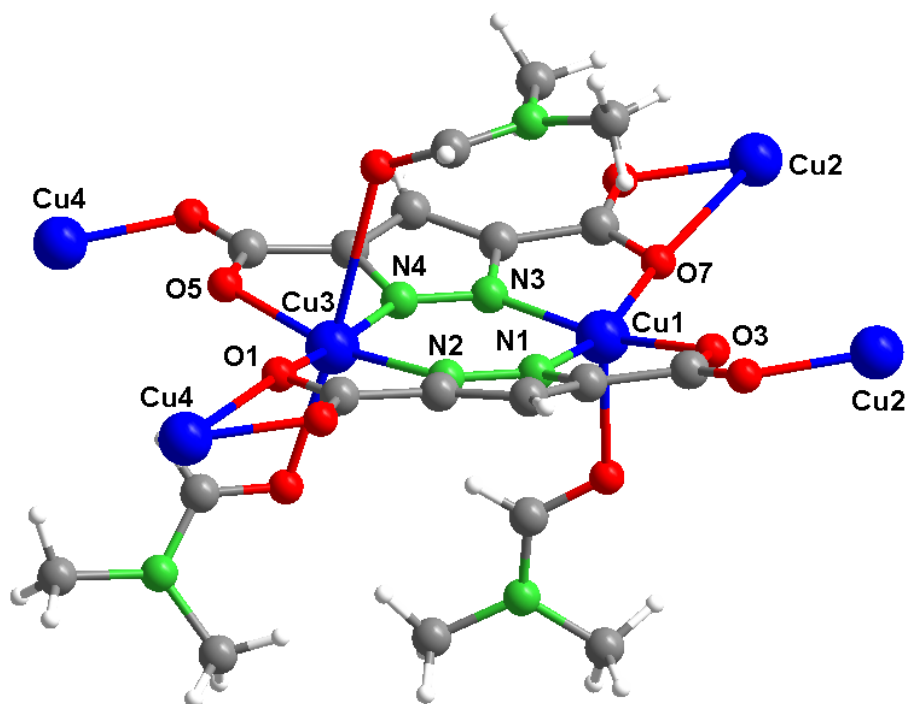


Fig. S5. A ball and stick presentation of the coordination environment of the six-membered bimetallic ring in MOF-648 ($[\text{Cu}_{12}(\text{L})_8 \cdot (\text{DMF})_9] \cdot (\text{DMF})_2(\text{H}_2\text{O})_2$). Color code: Cu, blue; N, green; O, red; C, gray; H, white. Selected atom labels are shown.

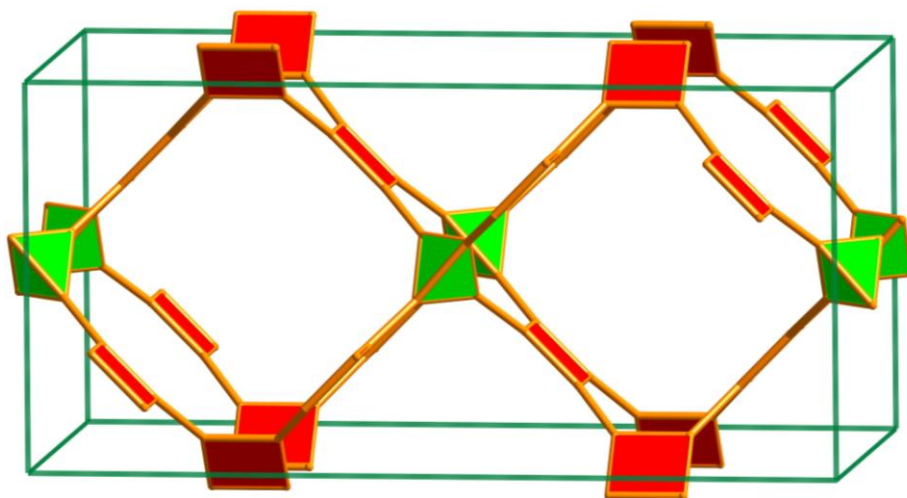


Fig. S6. Schematic presentation of an augmented trinodal 4-connected net (**sbr**) having the minimum number of kinds of edge (2) for the trinodal net as observed in MOF-648.

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Systre^[S7] file for sbr in MOF-648:

CRYSTAL

NAME sbr

GROUP Cmma

CELL 4.61883 2.30925 2.30954 90.0000 90.0000 90.0000

NODE 1 4 0.37500 0.25000 0.25000

NODE 2 4 0.00000 0.00000 0.50000

NODE 3 4 0.25000 0.00000 0.00000

EDGE 2 0.12500 -0.25000 0.25000

EDGE 3 0.12500 0.25000 -0.25000

END

Section S4 Powder X-Ray Diffraction Patterns

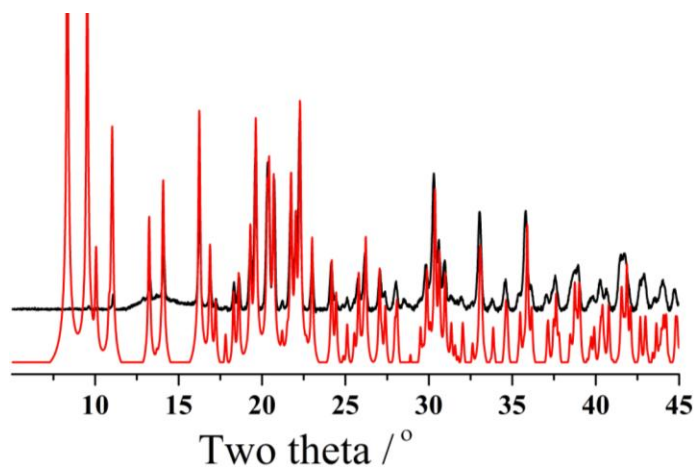


Fig. S7. Powder X-ray diffraction patterns: simulated from the single X-ray crystal structure of MOF-647A (red) and as-prepared MOF-647A (black).

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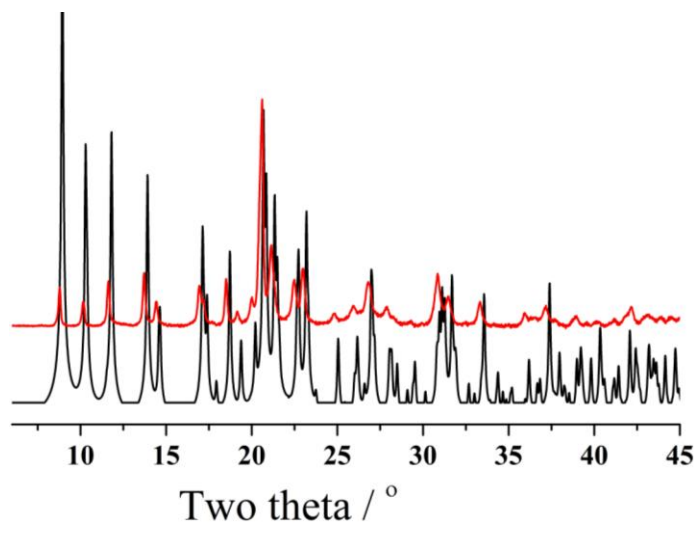


Fig. S8. Powder X-ray diffraction patterns: simulated from the X-ray single crystal structure of MOF-647B (black) and as-prepared MOF-647B (red).

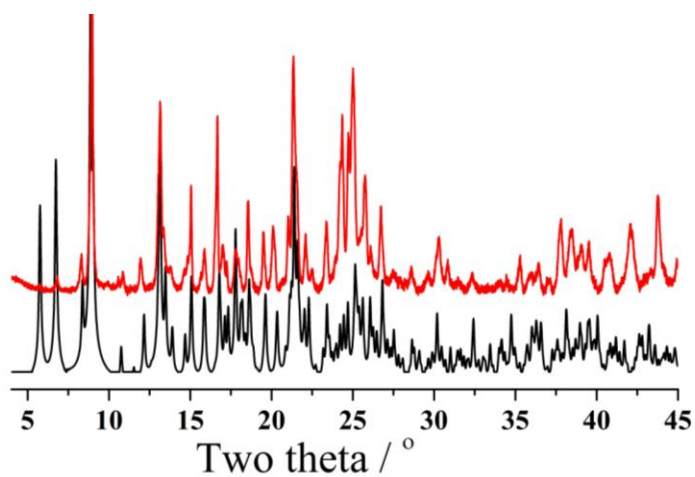


Fig. S9. Powder X-ray diffraction patterns for the simulation from the single crystal structure of MOF-648 (black), as-prepared MOF-648 (red).

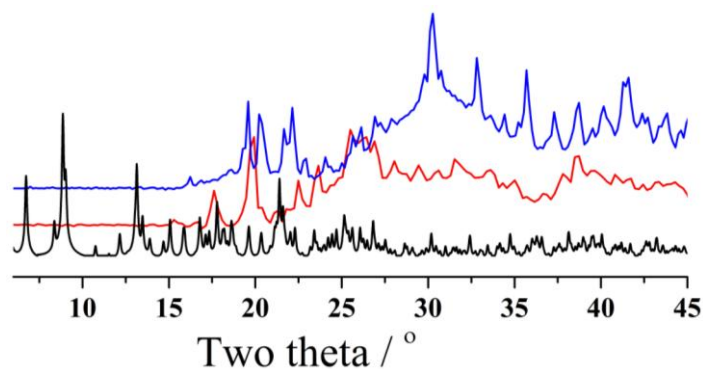


Fig. S10. Powder X-ray diffraction patterns for the simulation from the single crystal structure of MOF-648 (black), activated material prepared after degassing the acetone exchanged (for 3 d) material at 80 °C for 4 h (red) and the material obtained after resolution of the activated sample with DMF for 24 h and at room temperature (blue).

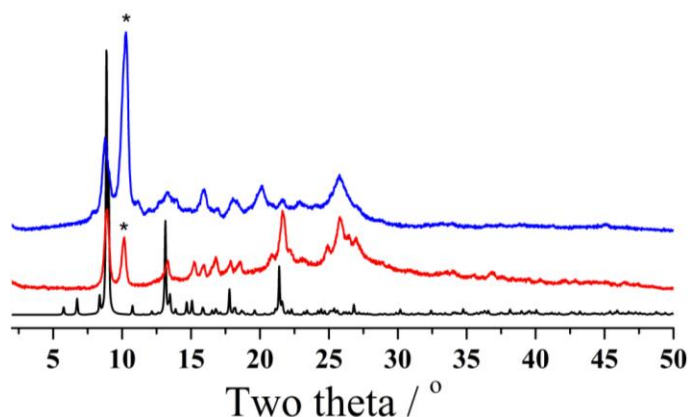


Fig. S11. Powder X-ray diffraction patterns for the simulation from the single crystal structure of MOF-648 (black), material prepared after SCD following acetone exchange for 3 d (red), the material prepared after degassing the SCD material at 50 °C for 3 h (blue). Note that the new and relatively low intensity peak at $2\theta = 10.2^\circ$ (marked with an asterisk) which appears after SCD activation becomes more intense after heating at 50 °C whereas simultaneously the intense peak around $2\theta = 8.9^\circ$ (for [102] and [111] reflections) goes down.

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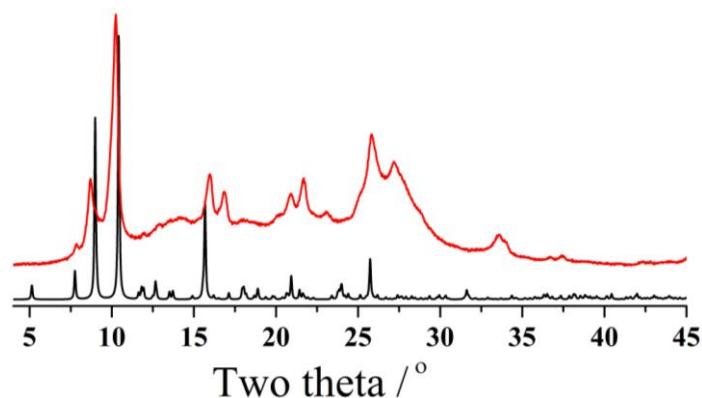


Fig. S12. Powder X-ray diffraction patterns for the simulation from the single crystal structure of MOF-648 (black) with modified cell parameters ($a = 17.2 \text{ \AA}$, $b = 15.2 \text{ \AA}$ and $c = 19.5 \text{ \AA}$) assuming that the space group (orthorhombic, $Pbcm$) was unaltered while the crystal lattice was compressed along the c -axis throughout the activation process and the material was prepared after degassing the SCD material at $50 \text{ }^\circ\text{C}$ for 3 h (red).

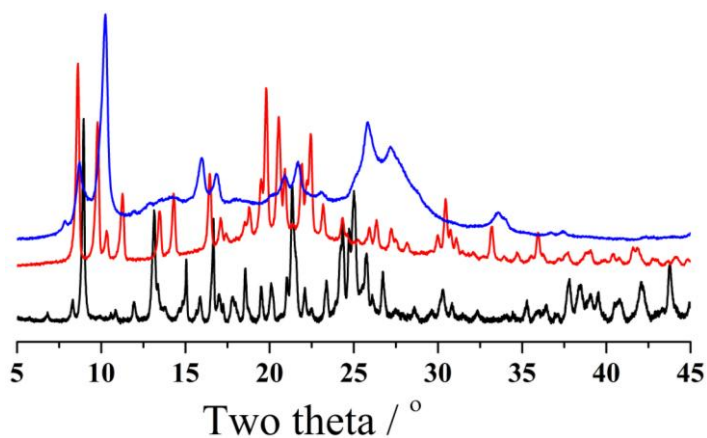


Fig. S13. Powder X-ray diffraction patterns for the as-prepared MOF-648 (black), the material prepared after degassing the SCD material at $50 \text{ }^\circ\text{C}$ for 3 h (blue) and the material obtained after resolution of the activated sample with DMF (red).

Section S5 Thermal Gravimetric Analysis

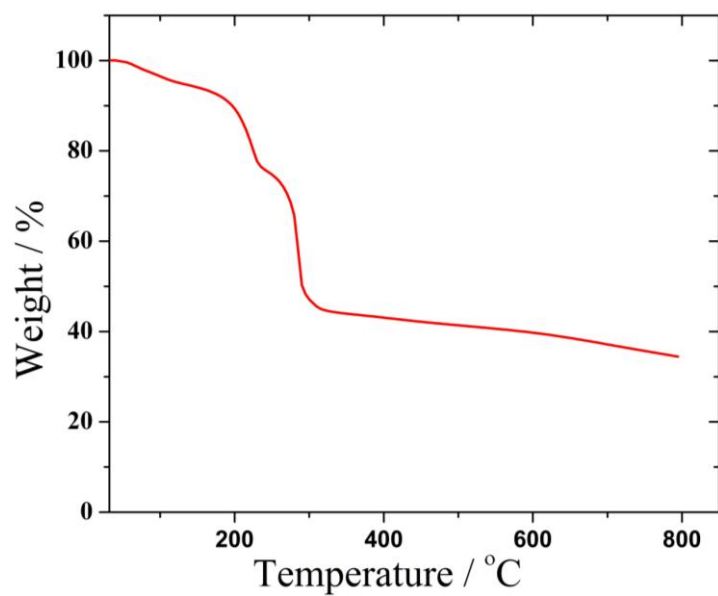


Fig. S14. TGA trace of as-synthesized MOF-647A.

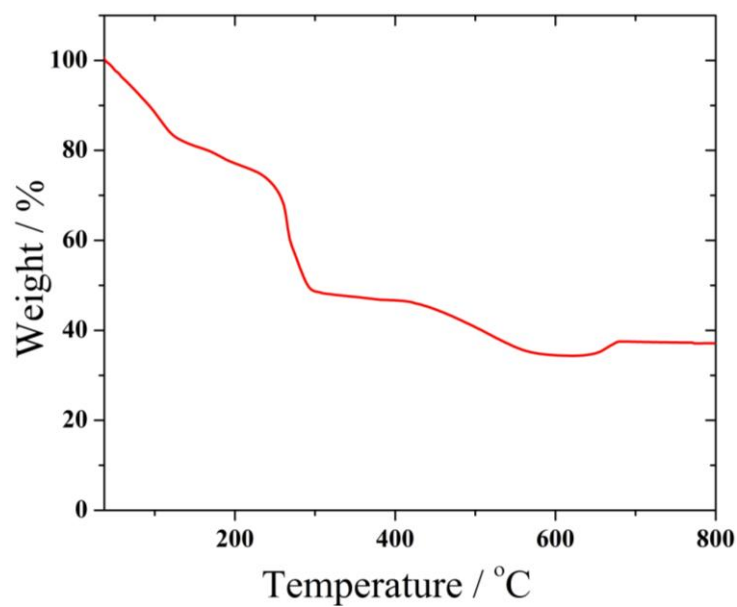


Fig. S15. TGA trace of as-synthesized MOF-647B.

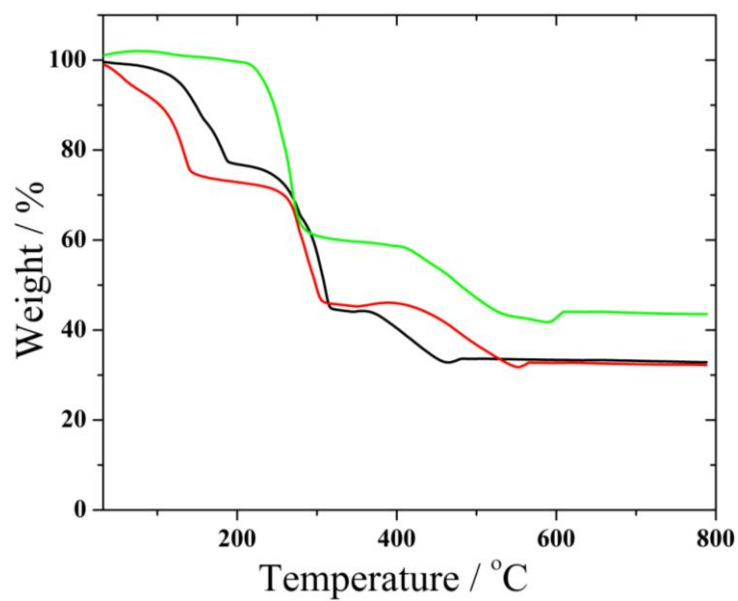


Fig. S16. TGA traces of as-synthesized MOF-648 (black), acetone exchanged for 3 d (red) and the activated material obtained after degassing the acetone exchanged material at 50-70 °C for 4 h.

Section S6 Gas Adsorption Measurements

Low-pressure N₂, H₂ and CO₂ adsorption measurements were performed on an Autosorb-1 (Quantachrome) volumetric analyzer.^[S8] The samples were outgassed to 10⁻⁶ torr. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. Liquid N₂ bath was used for adsorption measurements at 77 K. Ultra-high-purity grade He, N₂, H₂ and CO₂ were used throughout the adsorption experiments.

For porosity measurements, as-synthesized MOF-648 was immersed in acetone for 24 h, during which the activation solvent was replenished three times. The sample was evacuated with supercritical CO₂ in a Tousimis Samdri PVT-3D critical point dryer.^[S9,S10] Briefly, the acetone-containing sample was placed in the chamber and acetone was exchanged with liquid CO₂. After that the chamber containing the sample and liquid CO₂ was heated up around 40 °C and kept under the supercritical condition (typically 1300 psi) for 1 h. The CO₂ was slowly vented (ca. 1 h) from the chamber at around 40 °C. After the bleeding, the sample was degassing at 45 °C for 24 h to yield porous material.

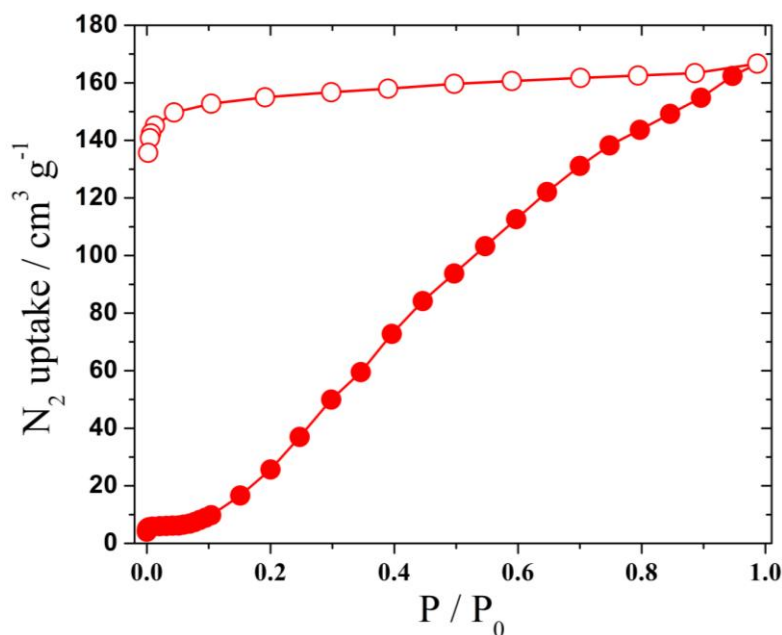


Fig. S17. N₂ isotherm of MOF-648 measured at 77 K. Filled and open circles represent adsorption and desorption branches, respectively. Connecting traces are guides for the eye.

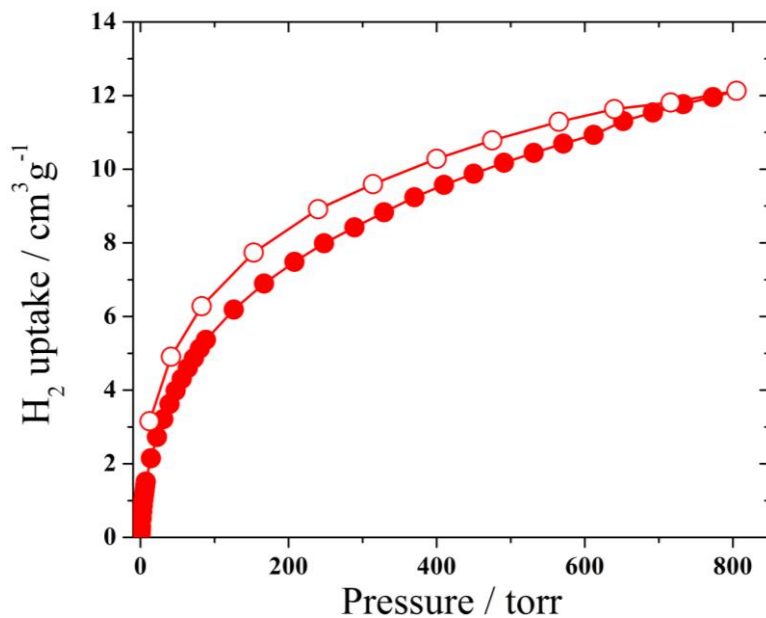


Fig. S18. H₂ isotherm of the activated MOF-648 measured at 77 K. Filled and open circles represent adsorption and desorption branches, respectively. Connecting traces are guides for the eye.

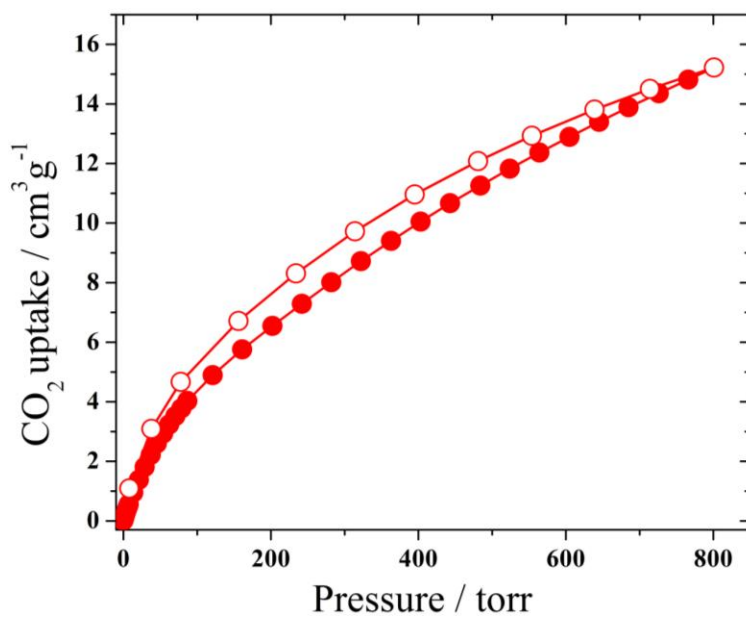


Fig. S19. CO₂ isotherm of the activated MOF-648 measured at 298 K. Filled and open circles represent adsorption and desorption branches, respectively. Connecting traces are guides for the eye.

Section S7 References

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